



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification <sup>7</sup> : <b>C07F 13/00, 15/00, 15/02, 15/04 // C08F 10/00</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 00/08034</b></p> <p>(43) International Publication Date: 17 February 2000 (17.02.00)</p>
<p>(21) International Application Number: PCT/GB99/02498</p> <p>(22) International Filing Date: 30 July 1999 (30.07.99)</p> <p>(30) Priority Data: 9817004.6 6 August 1998 (06.08.98) GB</p> <p>(71) Applicant (for all designated States except US): BP CHEMICALS LIMITED [GB/GB]; Britannic House, 1 Finsbury Circus, London EC2M 7BA (GB).</p> <p>(72) Inventors; and (75) Inventors/Applicants (for US only): GIBSON, Vernon, Charles [GB/GB]; Flat 2, 46 Prince's Gate, Exhibition Road, London SW7 2QA (GB). McTAVISH, Stuart, James [GB/GB]; Maisonette Flat, 475 Fulham Road, London SW6 1HL (GB).</p> <p>(74) Agent: SMITH, Julian, Philip, Howard; BP International Limited, Group Patents &amp; Agreements, Chertsey Road, Sunbury-on-Thames, Middlesex TW16 7LN (GB).</p>		<p>(81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published With international search report.</p>
<p>(54) Title: PREPARATION OF POLYMERISATION CATALYSTS</p> <div style="display: flex; justify-content: space-around; align-items: center;"> <div data-bbox="451 1184 867 1415"> <p style="text-align: center;">(B)</p> </div> <div data-bbox="1023 1213 1295 1402"> <p style="text-align: center;">Ligand (B)</p> </div> </div> <p>(57) Abstract</p> <p>A process is described for producing a transition metal complex of formula (B) wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand (B) and (2) a compound of the formula M[T]-(T/b)X. The complex has utility as a catalyst for the polymerisation of 1-olefins.</p>		

**FOR THE PURPOSES OF INFORMATION ONLY**

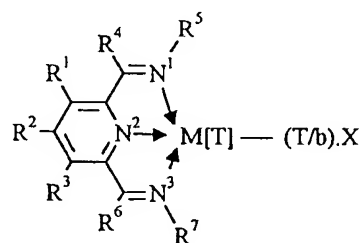
Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

### PREPARATION OF POLYMERISATION CATALYSTS

The present invention relates to a novel process for preparing transition metal compounds used as polymerisation catalysts.

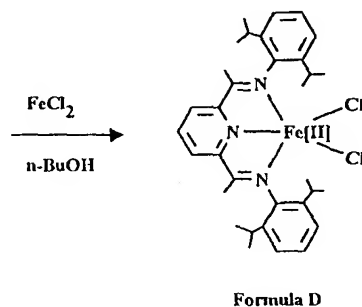
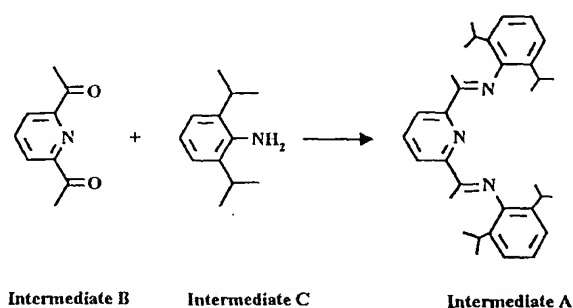
The use of certain transition metal compounds to polymerise 1-olefins, for example, ethylene, is well established in the prior art. The use of Ziegler-Natta catalysts, for example, those catalysts produced by activating titanium halides with organometallic compounds such as triethylaluminium, is fundamental to many commercial processes for manufacturing polyolefins. In recent years the use of certain metallocene catalysts (for example biscyclopentadienylzirconiumdichloride activated with alumoxane) has provided catalysts with potentially high activity and capable of providing an improved distribution of the comonomer units. Most recently, WO98/27124 has disclosed that ethylene may be polymerised by contacting it with certain iron or cobalt complexes of selected 2,6-pyridinecarboxaldehydebis(imines) and 2,6-diacylpyridinebis(imines); and our own copending application WO 99/12981 has disclosed novel nitrogen-containing transition metal compounds comprising the skeletal unit depicted in Formula B:



Formula B

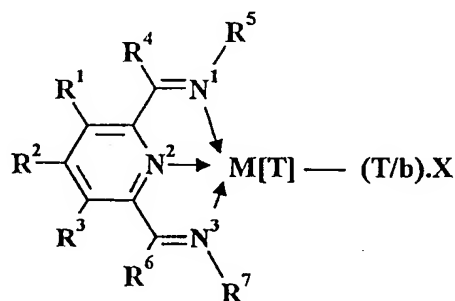
wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.

The above transition metal complexes are disclosed as being made by first forming the ligand (eg Examples 1 to 6 of WO 98/27124) and then separately reacting the ligand with the desired metal salt such as FeCl<sub>2</sub> or CoCl<sub>2</sub> (eg Examples 7 to 17 of WO 98/27124) to form the complex. This route is also exemplified in WO 99/12981, for example in the synthesis of 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub> (Formula D below), where the reaction scheme is shown as follows:



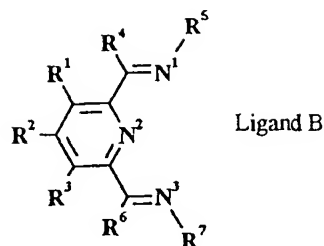
Hitherto, it has been considered necessary to complete the reaction between Intermediates B and C to form Intermediate A (the ligand), and to isolate Intermediate A from Intermediates B and C prior to reacting with the transition metal compound to form the transition metal complex compound (Formula B). However we have now discovered that this two step process can in fact be performed as a single stage reaction, using, for example, a single reaction vessel. This provides substantial process and economic advantages.

Accordingly a first aspect of the present invention provides a process for producing a transition metal complex of the formula



Formula B

wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand B

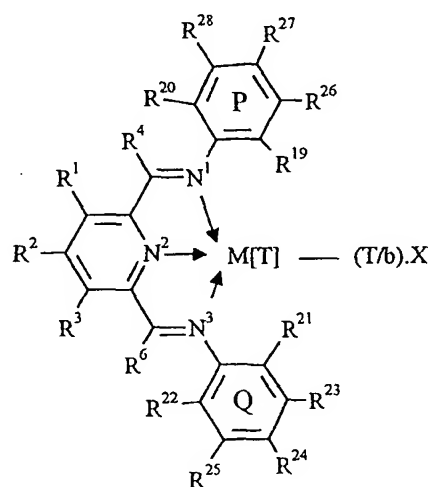


and (2) a compound of the formula  $M[T]-(T/b)X$ .

The reaction is preferably carried out in a single reaction vessel.

In the process of the present invention, the final product is obtained directly in a single stage reaction, without the need for any additional process steps: however at a molecular level the reaction may of course still proceed through more than one step.

Preferred transition metal complexes to be made by the process of the present invention comprise the skeletal unit depicted in Formula Z:



Formula Z

wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the

- valency of the atom or group X;  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more of  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted
- 5 heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents; with the proviso that at least one of  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  is hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl when neither of the ring systems P and Q forms part of a polyaromatic fused-ring system. In this particular aspect of the present invention, in the case that neither of the ring systems
- 10 P and Q forms part of a polyaromatic ring system, it is preferred that at least one of  $R^{19}$  and  $R^{20}$ , and at least one of  $R^{21}$  and  $R^{22}$  is selected from hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, and most preferably each of  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  is selected from hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl. The atom or group represented by
- 15 X is preferably halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate, hydrocarbyl, substituted hydrocarbyl and heterohydrocarbyl. Examples of such atoms or groups are chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.
- 20 Subject to the foregoing provisos regarding  $R^{19}$ ,  $R^{20}$ ,  $R^{21}$  and  $R^{22}$  in Formula Z,  $R^1$  to  $R^4$ ,  $R^6$  and  $R^{19}$  to  $R^{28}$  in the compounds depicted in Formulae B and Z of the present invention are preferably independently selected from hydrogen and  $C_1$  to  $C_8$  hydrocarbyl, for example, methyl, ethyl, n-propyl, n-butyl, n-hexyl, and n-octyl. In Formula B,  $R^5$  and  $R^7$  are preferably independently selected from substituted or
- 25 unsubstituted alicyclic, heterocyclic or aromatic groups, for example, phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5-dichloro-2,6-diethylphenyl, and
- 30 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl and pyridinyl.

The ring systems P and Q in Formula Z are preferably independently 2,6-hydrocarbylphenyl or fused-ring polyaromatic, for example, 1-naphthyl, 2-naphthyl, 1-

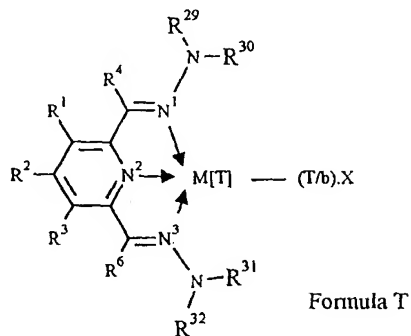
phenanthrenyl and 8-quinolinylnyl.

A further aspect of the present invention provides process for producing a transition metal complex having the Formula T:

5

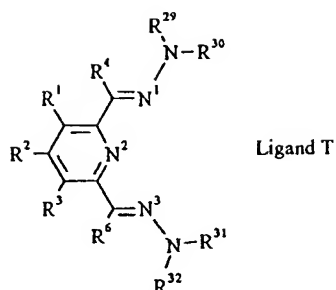
10

15



wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV],  
 20 Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded  
 to the transition metal M; T is the oxidation state of the transition metal M and b is the  
 valency of the atom or group X; R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>29</sup> to R<sup>32</sup> are independently selected  
 from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or  
 substituted heterohydrocarbyl; when any two or more of R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>29</sup> to R<sup>32</sup> are  
 25 hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted  
 heterohydrocarbyl, said two or more can be linked to form one or more cyclic  
 substituents,  
 comprising reacting together in a single stage reaction components comprising (1)  
 precursors capable of forming Ligand T





and (2) a compound of the formula  $M[T]-(T/b)X$ .

10        Examples of complexes which may be made by the process of the invention include 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridine(2,6-diisopropylanil)CoCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,6-dimethylanil)FeCl<sub>2</sub>, and 2,6-diacetylpyridinebis(2,4-dimethylanil)FeCl<sub>2</sub>.

15        FeCl<sub>2</sub>.

In the process of the present invention it is preferred that the components (1) and (2) of the reaction are brought together substantially simultaneously. However, if desired, they may be brought together in quick succession in any order.

20        Preferably the reaction between components (1) and (2) is carried out in the presence of an acidic catalyst. Examples of acidic catalysts include glacial acetic acid, p-toluenesulphonic acid and formic acid.

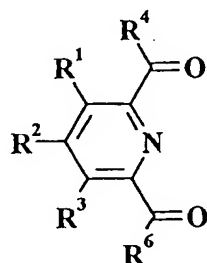
It is preferred to carry out the reaction in the presence of a liquid diluent. Most preferably the diluent is a solvent for one or more of the components of the reaction. Examples of suitable liquid diluents are liquid hydrocarbons, for example toluene, xylene, hexane and cyclohexane, or alcohols, for example, ethanol, isopropanol or 1-butanol.

25        butanol..

The reaction is preferably carried out at temperatures between 0°C and 150°C. Preferably the reaction is heated, typically to a temperature between 50°C and 130°C, more usually to between 70 to 110°C.

30        The time for the reaction may be, for example, from 5 minutes to 72 hours, though it is more usually between 12 and 48 hours, typically 18 to 36 hours.

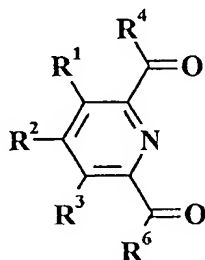
The ligand precursors employed in the reaction process of the present invention to make the "Ligand B" preferably comprise a compound of the Formula K



Formula K

plus compounds  $H_2NR^5$  and  $H_2NR^7$ , where  $R^1$  to  $R^7$  are as defined above. When  $R^5$  and  $R^7$  are the same, two equivalents of the same amine compound are of course used. When  $R^5$  and  $R^7$  are the different and two amines are used, a mixture of products may be obtained, with  $R^5$  and  $R^7$  being either the same or different on an individual molecule.

The ligand precursors employed in the reaction to make the "Ligand T" preferably comprise a compound of the Formula K



Formula K

plus compounds  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$ , where  $R^1$  to  $R^4$ ,  $R^6$ ,  $R^{29}$ ,  $R^{30}$ ,  $R^{31}$  and  $R^{32}$  are as defined above. When  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$  are the same, two equivalents of the same amine compound are used. When  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$  are the different, a mixture of products may be obtained, with  $-NR^{29}R^{30}$  and  $-NR^{31}R^{32}$  being either the same or different on an individual molecule.

In the process of the present invention, M and X in the compound of the formula  $M[T]-(T/b)X$  [component (2)] are as defined in the Formulae B, Z and T as set out above. Examples of compounds of the formula  $M[T]-(T/b)X$  are  $FeCl_2$ ,  $MnCl_2$ ,  $CoCl_2$ ,  $FeBr_2$ ,  $CoBr_2$  and  $FeCl_3$ . Preferred metals M[T] are Fe[II], Fe[III], Co[II] and Co[III].

5 The process of the present invention can be used to produce mixtures of complexes containing two or more different transition metals, for example, by employing two or more different transition metal compounds of formula  $M[T]-(T/b)X$  as the component (2).

The complexes made according to the process of the invention may be used  
 10 directly as polymerisation catalysts. Alternatively they may be combined with an activator. The activator compound is suitably selected from organoaluminium compounds and hydrocarbylboron compounds. Suitable organoaluminium compounds include trialkylaluminium compounds, for example, trimethylaluminium, triethylaluminium, tributylaluminium, tri-n-octylaluminium, ethylaluminium dichloride,  
 15 diethylaluminium chloride and alumoxanes. Alumoxanes are well known in the art as typically the oligomeric compounds which can be prepared by the controlled addition of water to an alkylaluminium compound, for example trimethylaluminium. Such compounds can be linear, cyclic or mixtures thereof. Commercially available alumoxanes are generally believed to be mixtures of linear and cyclic compounds. The cyclic  
 20 alumoxanes can be represented by the formula  $[R^{16}AlO]_s$  and the linear alumoxanes by the formula  $R^{17}(R^{18}AlO)_s$  wherein s is a number from about 2 to 50, and wherein  $R^{16}$ ,  $R^{17}$ , and  $R^{18}$  represent hydrocarbyl groups, preferably  $C_1$  to  $C_6$  alkyl groups, for example methyl, ethyl or butyl groups.

Examples of suitable hydrocarbylboron compounds are  
 25 dimethylphenylammoniumtetra(phenyl)borate, trityltetra(phenyl)borate, triphenylboron, dimethylphenylammonium tetra(pentafluorophenyl)borate, sodium tetrakis[(bis-3,5-trifluoromethyl)phenyl]borate,  $H^+(OEt_2)[(bis-3,5-trifluoromethyl)phenyl]borate$ , trityltetra(pentafluorophenyl)borate and tris(pentafluorophenyl) boron.

30 The quantity of activating compound selected from organoaluminium compounds and hydrocarbylboron compounds for the process for making the polymerisation catalyst is easily determined by simple testing, for example, by the preparation of small test

samples which can be used to polymerise small quantities of the monomer(s) and thus to determine the activity of the produced catalyst. It is generally found that the quantity employed is sufficient to provide 0.1 to 20,000 atoms, preferably 1 to 2000 atoms of aluminium or boron per Fe, Co, Mn or Ru metal atom in the compound of Formula B.

5 If desired, the preparation of the polymerisation catalyst can be carried out in the same vessel as the preparation of the transition metal complex by the process of the present invention.

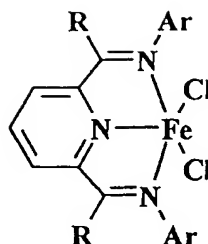
Catalysts made with complexes prepared according to the present invention can be unsupported or supported on a support material, for example, silica, alumina, or  
10 zirconia, or on a polymer or prepolymer, for example polyethylene, polystyrene, or poly(aminostyrene). If desired the catalysts can be formed *in situ* in the presence of the support material, or the support material can be pre-impregnated or premixed, simultaneously or sequentially, with one or more of the catalyst components. The catalysts can if desired be supported on a heterogeneous catalyst, for example, a  
15 magnesium halide supported Ziegler Natta catalyst, a Phillips type (chromium oxide) supported catalyst or a supported metallocene catalyst. Formation of the supported catalyst can be achieved for example by treating the transition metal compounds of the present invention with alumoxane in a suitable inert diluent, for example a volatile hydrocarbon, slurring a particulate support material with the product and evaporating  
20 the volatile diluent. The quantity of support material employed can vary widely, for example from 100,000 to 1 grams per gram of metal present in the transition metal compound.

If it is desired to use the catalyst on a support material (see below), this can be achieved, for example, by preforming the catalyst system comprising the transition metal  
25 complex and the activator and impregnating the support material preferably with a solution thereof, or by introducing to the support material one or more of the components simultaneously or sequentially.

### EXAMPLES

#### 30 Preparation of complexes

2,6-pyridyldiimine iron(II)dichloride complexes of the formula below were produced by the process of the invention.



- 1 R=H, Ar = 2,4,6-trimethylanil  
 2 R = Me, Ar = 2,4,6-trimethylanil  
 3 R = H, Ar = 2,6-diethylanil

### Example 1

#### Preparation of 1 - [2,6-dialdiminepyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

To a schlenk tube, under a nitrogen atmosphere, 2,6-pyridinedicarboxaldehyde (1.2eqs, 0.054g, 0.397mmol), anhydrous iron(II)dichloride (1eq, 0.042g, 0.331mmol) and 2,4,6-trimethylaniline (2.5eq, 0.12ml, 0.828 mmol) were added followed by *n*-butanol (40ml, dry) to form a yellow suspension. The reaction mixture was heated at 80°C for 20h to produce a brown precipitate. Solvent removed at the pump and the residue washed, ether (6x30ml) to yield a brown solid (0.101g, 62%),

1. FAB<sup>+</sup> MS *m/z* 495 [M<sup>+</sup>], 460 [M<sup>+</sup>-Cl], 422 [M<sup>+</sup>-2Cl], 368 [M<sup>+</sup>-FeCl<sub>2</sub>].

IR ν(C=N) 1632cm<sup>-1</sup>. No other C=N peaks were observed in the IR.

### Example 2

#### Preparation of 2 - [2,6-diacetylpyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

To a schlenk tube, under a nitrogen atmosphere, 2,6-diacetylpyridine (1.2eq, 0.054g, 0.397mmol), anhydrous iron(II)dichloride (1eq, 0.042g, 0.331mmol), 2,4,6-trimethylaniline (2.5eq, 0.12ml, 0.828 mmol) and glacial acetic acid (3 drops, catalyst) were added followed by *n*-butanol (40ml, dry). The reaction mixture was heated at 80°C for 24h to produce a dark blue precipitate. Solvent removed at the pump and the residue washed, ether (4x30ml) to yield a dark blue solid (0.137g, 83%),

2. FAB<sup>+</sup> MS *m/z* 523 [M<sup>+</sup>], 488 [M<sup>+</sup>-Cl], 453 [M<sup>+</sup>-2Cl]

Example 3Preparation of 3- [2,6-diacetylpyridinebis(2,6-diethylanil) FeCl<sub>2</sub>]

Anhydrous iron(II)dichloride (0.095g, 0.750mmol) 2,6-pyridinedicarboxaldehyde (1.2eq,  
 5 0.122g, 0.900mmol), and 2,6-diethylaniline (2.5eq, 0.310ml, 1.875 mmol) were added to  
 a Schlenk tube, followed by n-butanol (40ml), and were heated at 80°C for 48h. A green  
 precipitate appeared after 10min. Solvent was removed at the pump to yield, upon  
 washing with ether (4 x 40ml), a green solid. FAB<sup>+</sup> MS *m/z* 523 [M<sup>+</sup>], 488 [M<sup>+</sup>-Cl], 453  
 [M<sup>+</sup>-2Cl].

10

Polymerisation using complexes prepared above

To a Schlenk tube, catalyst (0.01mmol) and toluene (40ml, dry) were added  
 followed by methylalumoxane (10%w/w in toluene, 100eq, 0.65ml, 1.00mmol) to form  
 an orange solution. The Schlenk tube was placed in a water bath at ambient temperature.  
 15 Ethylene atmosphere (1 bar) was passed over the solution for 30 minutes. The reaction  
 was then quenched by addition of dilute HCl (40ml), and the resulting polymer filtered  
 and washed with methanol (3x50ml) to yield, upon drying in vacuum oven, solid  
 polyethylene.

20 Example 4Polymerisation using 1 - [2,6-dialdiminepyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

Complex 1, (0.01mmol, 4.96mg), yielded 6.20g polyethylene giving an activity of  
 1240 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup>.

PE, M<sub>w</sub>= 46000, PDI= 18.0, M<sub>PK</sub>= 1400

25

Example 5Polymerisation using 2 - [2,6-diacetylpyridinebis(2,4,6-trimethylanil) FeCl<sub>2</sub>]

Complex 2, (0.01mmol, 5.24mg), yielded 4.35g polyethylene giving an activity of  
 870 gmmol<sup>-1</sup>h<sup>-1</sup>bar<sup>-1</sup>.

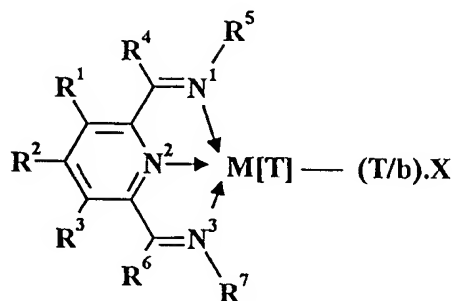
30

PE, M<sub>w</sub>= 80 000, PDI= 21.0, M<sub>PK</sub>= 70 000.

These results show that the process of the invention provides catalysts which are as  
 effective as those produced by the known two-stage process.

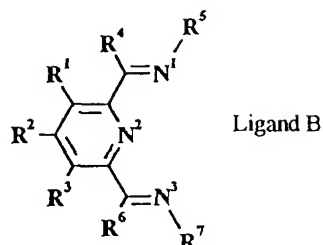
## Claims:

1. Process for producing a transition metal complex of the formula



Formula B

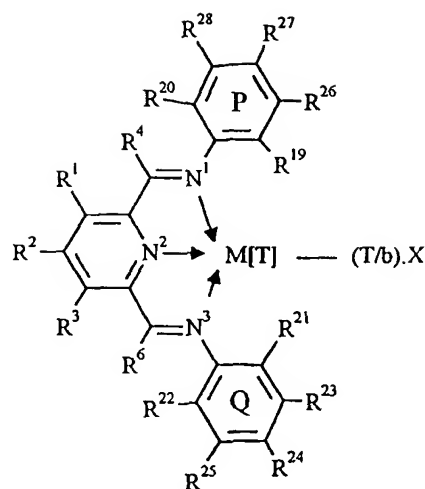
- wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV], Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded to the transition metal M; T is the oxidation state of the transition metal M and b is the valency of the atom or group X; R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, R<sup>6</sup> and R<sup>7</sup> are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; and when any two or more of R<sup>1</sup> - R<sup>7</sup> are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents;
- comprising reacting together in a single stage reaction components comprising (1) precursors capable of forming Ligand B



and (2) a compound of the formula  $M[T]-(T/b)X$ .

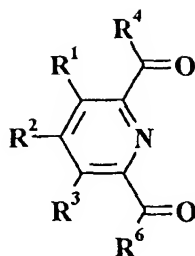
2. Process according to claim 1 which is carried out in a single reaction vessel.
- 10 3. Process according to claim 1 or 2 wherein components (1) and (2) of the reaction are brought together substantially simultaneously.
4. Process according to any preceding claim wherein the reaction between components (1) and (2) is carried out in the presence of an acidic catalyst.
5. Process according to claim 4 wherein the acidic catalyst comprises glacial acetic acid, p-toluenesulphonic acid or formic acid.
- 15 6. Process according to any preceding claim wherein the reaction is carried out in the presence of a liquid diluent.
7. Process according to claim 6 wherein the diluent comprises toluene, xylene, hexane, cyclohexane, ethanol, isopropanol or 1-butanol.
- 20 8. Process according to any preceding claim wherein the reaction is carried out at a temperature of from 50°C to 130°C.
9. Process according to any preceding claim wherein the transition metal complex has the skeletal unit depicted in Formula Z:





Formula Z

- 15 wherein M is Fe[II], Fe[III], Co[I], Co[II], Co[III], Mn[I], Mn[II], Mn[III], Mn[IV],  
 Ru[II], Ru[III] or Ru[IV]; X represents an atom or group covalently or ionically bonded  
 to the transition metal M; T is the oxidation state of the transition metal M and b is the  
 valency of the atom or group X; R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>19</sup> to R<sup>28</sup> are independently selected  
 20 from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or  
 substituted heterohydrocarbyl; when any two or more of R<sup>1</sup> to R<sup>4</sup>, R<sup>6</sup> and R<sup>19</sup> to R<sup>28</sup> are  
 hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted  
 heterohydrocarbyl, said two or more can be linked to form one or more cyclic  
 substituents; with the proviso that at least one of R<sup>19</sup>, R<sup>20</sup>, R<sup>21</sup> and R<sup>22</sup> is hydrocarbyl,  
 substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl when  
 25 neither of the ring systems P and Q forms part of a polyaromatic fused-ring system.
10. Process according to claim 9 wherein the reactants comprise  
 (1a) a compound of the Formula K

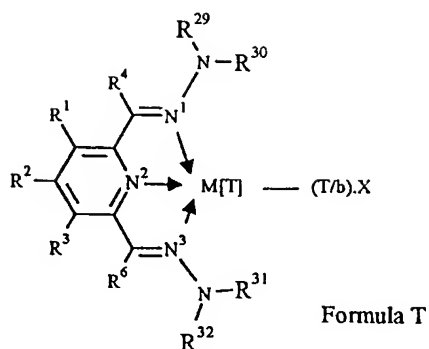


Formula K

- 10 (1b) compounds having the formulae  $H_2NR^5$  and  $H_2NR^7$ , and  
 (2) a compound of the formula  $M[T]-(T/b)X$ .
11. Process according to any preceding claim wherein  $R^5$  and  $R^7$  are independently selected from phenyl, 1-naphthyl, 2-naphthyl, 2-methylphenyl, 2-ethylphenyl, 2,6-diisopropylphenyl, 2,3-diisopropylphenyl, 2,4-diisopropylphenyl, 2,6-di-n-
- 15 butylphenyl, 2,6-dimethylphenyl, 2,3-dimethylphenyl, 2,4-dimethylphenyl, 2-t-butylphenyl, 2,6-diphenylphenyl, 2,4,6-trimethylphenyl, 2,6-trifluoromethylphenyl, 4-bromo-2,6-dimethylphenyl, 3,5 dichloro-2,6-diethylphenyl, and 2,6-bis(2,6-dimethylphenyl)phenyl, cyclohexyl and pyridinyl.
12. Process according to any of claims 1 to 8 wherein the transition metal complex
- 20 has the skeletal unit depicted in Formula T:

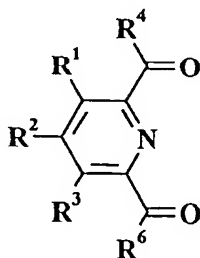
25

5



- 10 wherein  $R^{29}$  to  $R^{32}$  are independently selected from hydrogen, halogen, hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl; when any two or more thereof are hydrocarbyl, substituted hydrocarbyl, heterohydrocarbyl or substituted heterohydrocarbyl, said two or more can be linked to form one or more cyclic substituents.
- 15 13. Process according to claim 12 wherein the reactants comprise  
(1a) a compound of the Formula K

20



Formula K

25

- (1b) compounds having the formulae  $H_2N-NR^{29}R^{30}$  and  $H_2N-NR^{31}R^{32}$ , and  
(2) a compound of the formula  $M[T]-(T/b).X$ .
14. Process according to any preceding claim wherein X comprises halide, sulphate, nitrate, thiolate, thiocarboxylate,  $BF_4^-$ ,  $PF_6^-$ , hydride, hydrocarbyloxy, carboxylate,  
30 hydrocarbyl, substituted hydrocarbyl or heterohydrocarbyl.

15. Process according to claim 14 wherein X comprises chloride, bromide, methyl, ethyl, propyl, butyl, octyl, decyl, phenyl, benzyl, methoxide, ethoxide, isopropoxide, tosylate, triflate, formate, acetate, phenoxide and benzoate.
16. Process according to any preceding claim wherein M[T] comprises Fe[II],
- 5 Fe[III], Co[II] or Co[III].
17. Process according to any of claims 1 to 11, wherein the transition metal complex comprises 2,6-diacetylpyridinebis(2,6-diisopropylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-diacetylpyridine(2,6-diisopropylanil)CoCl<sub>2</sub>, 2,6-diacetylpyridinebis(2,4,6-trimethylanil)FeCl<sub>2</sub>, 2,6-
- 10 diacetylpyridinebis(2,6-dimethylanil)FeCl<sub>2</sub>, or 2,6-diacetylpyridinebis(2,4-dimethylanil)FeCl<sub>2</sub>.

## INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/GB 99/02498

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07F13/00 C07F15/00 C07F15/02 C07F15/04 //C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	BLACK, DAVID ST. CLAIR ET AL: "Template synthesis of metal complexes containing new macrocyclic ligand systems" TETRAHEDRON LETT. (1978), (31), 2835-6 , 1978, XP002117950 the whole document	1
A	WO 98 27124 A (E.I. DU PONT DENOURS AND COMPANY) 25 June 1998 (1998-06-25) cited in the application examples	1

☐ Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&amp;" document member of the same patent family

Date of the actual completion of the international search

7 October 1999

Date of mailing of the international search report

21/10/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Rinkel, L

# INTERNATIONAL SEARCH REPORT

Information on patent family members

In tional Application No

PCT/GB 99/02498

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9827124 A	25-06-1998	AU 5711098 A	15-07-1998
		EP 0946609 A	06-10-1999
		NO 992930 A	10-08-1999
<hr/>			